On the possibility of using differential cross section measurements for the electronic excitation of adsorbates by an electron beam, to determine the adsorbate orientation

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We show, by detailed electron–molecule scattering calculations, that the angular dependence of electron energy loss spectra in which an adsorbate is electronically excited can be used to identify the orientation of the molecule with respect to the surface and the nature of the final states. The calculations are exploratory and were carried out for an H_2 molecule. The transition amplitude for electron–molecule scattering is calculated by using the Schwinger variational principle with two open channels. The effects of the surface were introduced through a semiquantitative model which treats the surface as a partly reflecting, flat mirror.

I. INTRODUCTION

Several factors make the use of optical spectroscopy in surface science less prominent than in other areas of chemical physics: the system of interest are often submonolayers, the photon molecule cross sections can be small, and the use of high laser power is limited by surface heating. A remedy is provided by the fact that the cross sections for inelastic electron–molecule collisions substantially exceed those for photons, and surface science can obtain spectroscopic information by using electron energy loss spectroscopy.[1,2] While most of the existing work is concerned with vibrational spectroscopy, the experimental study of the electronic excitations of the adsorbate is also coming of age.[3–23] This activity has created a need for a theory of electron–adsorbate collisions which can assist the experimentalists in assigning the loss peaks, in using the spectra to determine the orientation of the molecule with respect to the surface, and, ultimately, in deciding which of the many electronic structure models for chemisorption is closest to reality. The role of theory and the specific theoretical problems to be addressed can be best defined by examing how these tasks are performed now.

A. A description of the key problems

1. The determination of the molecular orientation

The use of electronic EELS spectra to determine the orientation of an adsorbed molecule with respect to the surface relies on an adaptation[23] of a dipole selection rule which is widely used in interpreting vibrational EELS data.[1,2] This rule states[24,25] that the electrons scattered in a specular direction cannot excite the adsorbate's vibrational motion if the oscillating molecular dipole is parallel to the surface, and excites it with maximum efficiency if the dipole is perpendicular to the surface.

The simplest argument leading to this rule begins with the assumption that most of the electrons that are scattered inelastically in a nearly specular direction, end up in that situation because they interacted weakly with the molecule and were deflected only slightly by it. Classically this says that most of the electrons scattered in a near-specular direction had a large impact parameter with respect to the molecule. Thus, in surface science, the near-specular direction plays a role similar to that played by the near-forward direction in gas phase electron–molecule collisions.

If the impact parameter is larger than the size of the molecular charge distribution, the electron interacts primarily with the molecular dipole moment $\boldsymbol{\mu}$. If we expand the dipole in a power series with respect to the vibrational amplitude δQ the energy transfer from electrons to molecular vibrations takes place mainly through the term $\delta Q(\partial\boldsymbol{\mu}/\partial Q)\cdot\mathbf{E}$, where $\mathbf{E}$ is the electromagnetic field created at the position of the moelcule by the colliding electron. The dipole selection rules now follow for two reasons. First, at a metal surface the electron field $\mathbf{E}$ is nearly perpendicular to the surface because of the boundary conditions imposed by phenomenological electrodynamics.[26,27] Thus, the coupling $\mathbf{E}\cdot(\partial\boldsymbol{\mu}/\partial Q)$ is nearly zero if $\partial\boldsymbol{\mu}/\partial Q$ is parallel to the surface, and it is close to maximum if $\partial\boldsymbol{\mu}/\partial Q$ is perpendicular. Secondly, the solid surface is polarized by the presence of the molecular dipole. The electric field created outside the metal by this polarization charge is equal, according to phenomenological electrodynamics,[26,27] to the field created by the image of the molecular dipole with respect to the surface. Since the passing electron is affected by this polarization field, the total electron–molecule interaction energy is obtained by adding, to the interaction with the molecular dipole, the interaction with its image. For perpendicular dipoles the two

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terms have the same sign and the image term increases the total electron–molecule interaction energy. For a parallel dipole the two terms have opposite signs and the total interaction is nearly zero. The extension of these rules to electronic EELS[23] can be made by replacing the vibrating molecular dipole with an induced Drude dipole which oscillates at the electronic transition frequency and whose direction is given by the transition dipole of the chemisorbed molecule. The fact that the process of absorption (or emission) of electromagnetic energy by electronic excitations can be described by such classical dipoles can be derived quantum mechanically[28,29] and has been successfully used within a classical framework to study fluorescence[30] and resonant Raman scattering[31] by adsorbates, as well as other surface spectroscopies.[32]

Recent electonic EELS studies of adsorbed benzene[14,16,18] and pyridine[16,18–20] were carried out to test this selection rule. Experiments with gas phase molecules or with molecular crystals show that both pyridine and benzene have intense loss features in the region 4–10 eV, which can be assigned to $\pi \rightarrow \pi^*$ transitions.[33–35] The transition dipole for these excitations is parallel to that of the aromatic ring. The dipole selection rules hence predict that such transitions will not be observed in electronic EELS experiments if the molecular ring is parallel to the surface, and will be observable if the ring is perpendicular. The measurements of Netzer and Matthew[14] did not find any 7 eV loss feature for benzene on Pt(111) or on Ir(111).[16] Furthermore, Netzer, Berthel, and Matthew[16] find that the corresponding loss features are present for pyridine on Ir(111). Since there is evidence[16] that C_6H_6 is adsorbed with the ring parallel to the surface, and pyridine binds through the nitrogen atom with the ring perpendicular to the surface, these findings agree with the predictions made by the selection rule. A more convincing case has been made by Avouris, DiNardo, and Demuth[20] who used vibrational EELS to show that pyridine on Ag(111)[36] and Ni(100)[20] binds with the ring parallel to the surface at low coverage and stands up at high coverage. They then showed that the electronic EELS spectra of pyridine in these systems behave as expected on the basis of the dipole rules: the $\pi \rightarrow \pi^*$ transitions are observed only when the coverage is high enough to force pyridine to stand up.[20] However, we note that the experimental data can also be explained by assuming that when the ring of the aromatic molecules is parallel to the surface the π and π^* orbitals interact strongly[38,39] with those of the metal, forming joint orbitals. The interaction between the discrete levels of the molecule and the continuum formed by the orbitals of the solid can lead to a substantial broadening (and shifting) of the transition line shape,[37] since the lifetime of the excited electron in the molecular part of the orbital is very short. It is thus possible that these excitations are not observed in the electronic EELS spectra because they are broadened out of existence.

Moreover, under the usual conditions of EELS experiments, the theoretical arguments based on dipole selection rules do not really have much basis. The classical picture used above is valid only if the Born approximation[40] works and exchange effects are negligible.[40] This is the case only if the energy of the incident electron is very high (i.e., several hundred eV).[40] However, with one exception,[41] all EELS experiments are carried out at much lower kinetic energy. Furthermore, the dipole approximation is valid only if the momentum transfer to the molecule is rather small. This is true for electrons that arrived at the detector after being forward scattered by the molecule, and backscattered specularly by the surface, and have lost only a small fraction of their energy. If the energy transferred in the inelastic process is a substantial fraction of the incident energy or if the excitation is spin or dipole forbidden, the electron–molecule interaction cannot be described by representing the molecule by a dipole. Furthermore, as many model calculations show the image formulas are not valid for either low frequency[42] or high frequency[43] oscillating charges, located close to the surface, because the dielectric constant at the surface is not discontinuous and local,[44] as assumed by the phenomenological electrodynamics.

Therefore, we feel that if the dipole selection rule seems to work in the case of electronic EELS experiments, it is because it manages to be accurate beyond its expected limits of validity. Such an accidental validity makes the rules difficult to use since it lowers their reliability; one cannot consistently count on favorable accidents. Thus we are lead naturally to the main question of this paper: can we base the use of electronic EELS spectra to determine molecular orientations on calculations of inelastic differential electron–molecule scattering cross sections?

2. The assignment of the loss peaks

The limited experimental literature available shows that the assignment of an electronic loss peak to a specific transition is difficult even for simple adsorbates whose electron scattering behavior in gas phase is well known. For example, in the case of CO the losses in the 13–15 eV region were assigned to a $1\pi \rightarrow 2\pi^*$ transition (by Netzer and Matthew),[15] to a Rydberg excitation (by Rubloff and Freeouf,[11] and Chester *et al.*[8]), and to a $4\sigma \rightarrow 2\pi^*$ transition (by Akimoto *et al.*[12]). The assignment of an 8 eV peak, by Avouris *et al.*[12] to a $5\sigma \rightarrow 2\pi^*$ transition is accepted by Netzer *et al.*[17] only with some qualifications.

There are several reasons for these difficulties: binding to the surface can shift the peaks and broaden them, thus modifying their position and their relative intensity; chemisorption can induce new transitions (i.e., having no gas phase analog), such as the excitation of an electron from a molecular orbital into the empty orbitals of the metal; the substrate excitations can be modified by chemisorption (e.g., surface states and surface plasmons are modified by the presence of the adsorbate), a change that might be mistakenly taken to be the result of a molecular excitation; the selection rules can be affected by chemisorption causing a change in intensity as compared to those obtained in a gas phase measurement.

Thus, the next important question that the theory must address is whether detailed calculations of electron–molecule scattering can help in the identification of various transitions. What we have in mind is not the calculation of the energy of each transition, which in principle can be done by using the methods of quantum chemistry, but the use of elec-

tron scattering theory to determine the angular distribution of the scattered electrons for each final state, and its dependence on the incident energy and the angle of incidence. In fact group-theoretical arguments, and earlier studies of oriented H_2,[55] already suggest that the inelastic differential cross sections for electronic excitation of linear molecules should show a strong dependence on the angle of incidence of the electron. Our model studies indicate that the excitation of various final states leads to different angular distributions which can be used for final state identification. One of the few experimental studies of angle and energy dependence of the electronic EELS spectra, by Netzer *et al.*,[17] also shows a marked dependence of the spectrum on the angle of detection and the energy of incidence.

3. Detection of electronic structure changes caused by chemisorption

Traditionally the molecular information used to test the theories of the electronic structure has been obtained by optical spectroscopy. The electron is a finer probe since its scattering behavior depends on all the details of the molecular wave functions which determine the Coulomb and the exchange interaction of the electron with molecule. In principle it is much more likely that differential cross-section measurements of electron scattering can differentiate among various electronic structure models of the adsorbate than photon scattering measurements could. In practice however we are faced with a paradox: the electron is a better probe because it interacts strongly with the electrons of the molecule, but for the same reason its scattering properties are much more difficult to calculate than those of the photon. There are two ways of circumventing this situation. One is to use high energy electrons to make the electron molecule interaction relatively small; but this restricts the energy loss spectra primarily to dipole allowed transitions. In a sense we diminish the amount of detail that the electron probes, in order to make the interpretation easier and more reliable. For vibrational excitations the use of high energy electrons is possible but very difficult.[41] For electronic excitations this should be easier since the energies lost are larger and the peaks are broader than in the case of the vibrational excitations. However, we are not aware of the existence of any experiments in adsorbate–substrate studies.

The other way of using electron scattering to obtain information about the chemisorption induced changes in electronic structure of the molecule is to consider in detail the electron scattering by an "extended molecule" containing the adsorbate and several metal atoms. While such a calculation is possible, by the method used in this paper, it is sufficiently laborious to make it unwise to attempt it at this early stage. Thus, the calculations presented here do not include any chemisorption effects.

B. A brief presentation of the present work

After examining the experimental situation to define the key problems, we now briefly summarize our model studies. We inquire whether the electron–molecule differential cross section dependence on the angle of incidence and detection and on the initial energy, has pronounced trends that will permit identification of molecular orientation and facilitate peak assignment. Thus we treat scattering by the molecule carefully and reliably but, to keep the calculation feasible, we introduce the surface effects in a qualitative manner. Therefore, we assume that the surface acts as an imperfect, flat mirror which modifies the incident electron beam only before and after the collision with the molecule. The electron molecule scattering amplitude is computed by using the multichannel Schwinger variational principle developed by Takatsuka and McKoy.[54]

By the standards set by previous calculations of scattering cross sections for vibrational surface science, the present work is rather advanced. The pioneering and very important work of Evans and Mills[56] used oscillating point dipoles instead of molecules and used a representation of the surface that is essentially equivalent to ours. The electron dipole collision was treated by a distorted wave approximation (with the flat surface distorting the electron wave) and thus the whole procedure is valid at most for a near-specular high energy electron scattering only. Unfortunately this is a regime that has been avoided, for good experimental reasons, in most measurements. Subsequent improvements by Tong, Li, and Mills[57,58] used LEED theory[58] to incorporate the details of the electron scattering with the metal. The electron molecule scattering was treated in a LEED fashion also. Thus the treatment of the electron–molecule collision is of lower quality than in the present work, but the interaction with the metal is better described. We also mention the important paper by Davenport, Ho, and Schrieffer[59] who used the $X\alpha$ method of Dill and Dehmer[60] to compute the differential cross section for oriented diatomics whose rotation is frozen. The simplified electron–molecule interactions used in both LEED-like $X\alpha$ calculations can lead to inaccurate results in the differential cross section but there is as yet no evidence of any substantial failure[61]; while admittedly semiquantitative[61] the method is potentially very useful. While we believe that our treatment of the electron–molecule scattering is more accurate than that used in Refs. 56–59 we cannot make any direct comparison since these methods are not applicable to electronic EELS which is considered here.

Since chemisorption effects are not included in the present calculation, it is important that we examine what we have missed in so doing. First, chemisorption will distort the molecular charge distribution by changing its shape and shifting the charge. Moreover, a good electron scattering calculation is sensitive not only to the charge distribution but to the wave function as a whole, namely to the orbitals used to construct it and their occupation. These can also be modified by chemisorption. Such changes can occasionally have dramatic effects. For example, there is experimental evidence that CO chemisorption pulls the $2\pi^*$ orbital of CO below the vacuum level, forming occupied[45,46] and unoccupied[47,48] orbitals which are combinations of the $2\pi^*$ orbital with those of the metal. Since the $2\pi^*$ orbital of the free CO molecule leads to resonant electron scattering by CO,[49] the shift of this orbital below the vacuum level makes it inaccesible to the resonant scattering process. This is perhaps the

reason why the search for this resonance has been unsuccessful for chemisorbed CO.[50]

Second, the final molecular states are broadened by the fact that their lifetime is diminished. This is due to a variety of reasons: (a) the excited state emits a "photon" which is adsorbed by the metal. This effect is easily observed, for example, as fluorescence quenching.[30,32] (b) If the excited molecular electron is above the Fermi level, it is extremely likely that it will hop into the metal ionizing the molecule.[45] The ion is subsequently neutralized by an Auger process,[45,51] which generates the ground state of the molecule. Such processes are easily observed in metastable quenching spectroscopy.[45] (c) If the excited electron in the final state is below the Fermi level, the excited molecule can also be quenched by Penning ionization of the surface.[45] Surface-induced broadening was observed by Avouris, Schmeisser, and Demuth[52] and has been discussed by Persson and Avouris[53] on the bais of a simple Anderson–Newns model. Such calculations do not consider the effect of this broadening on the differential cross section.

Our main results are that the differential cross section in electronic EELS is very sensitive to the orientation of the molecule and to the nature of the final state. Therefore a combination of a calculation of the type carried out here and differential cross-section measurements is a useful addition to the existing EELS methodology. These calculations were carried out for an H_2 molecule, and are exploratory in nature. Since H_2 is a "nearly spherical" molecule its orientation is not very conspicuous to the incident electron; we expect that the trends observed here will be even more pronounced in the cross sections of H_2O, CO, and NH_3, which are presently under study.

II. THEORY

We calculate the scattering cross sections for electrons incident on a H_2 molecule held fixed (i.e., prevented from rotating) by the presence of the surface. In the simplified model used here we assume that chemisorption has not modified the electronic structure of the molecule and that the main effect of the surface is to act as an imperfect mirror which partially scatters the electron wave falling on it.

This simplified model requires that we have the transition amplitude for electron–molecule scattering in the absence of the surface. This is calculated by using a method developed by Takatsuka and McKoy[54] and the implementation for oriented molecules worked out by Lima *et al.*[55(a)] This procedure is outlined briefly in Sec. II A, where we indicate the physical factors taken into account, compare to previous theories, and comment on further extensions. The manner in which surface effects are included is presented in Sec. II B.

A. Electron scattering by the molecule

The transition amplitude $f(\mathbf{k}_f \leftarrow \mathbf{k}_i)$ for a collision in which the electron wave vector changes from $\mathbf{k}_i$ to $\mathbf{k}_f$ and the electronic wave function from the ground state S_i to a final state S_f is obtained from the multichannel Schwinger variational principle[55]

$$\mathbf{f}(\mathbf{k}_f \leftarrow k_i) = -(1/2\pi)\langle S_f|V|\psi_i^{(+)}\rangle\langle\psi_f^{(-)}|V|S_i\rangle \times\{\langle\psi_f^{(-)}|W - VG_p^{(+)}V|\psi_i^{(+)}\rangle\}^{-1}, \quad (2.1)$$

where $\psi_i^{(+)}$ and $\psi_i^{(-)}$ are trial scattering wave functions. The initial wave function S_i is given by

$$S_i(\mathbf{r}_1,...,\mathbf{r}_N,\mathbf{r}) = \Phi_i(\mathbf{r}_1,...,\mathbf{r}_N)\exp\{i\mathbf{k}_i\cdot\mathbf{r}\}, \quad (2.2)$$

where $\mathbf{r}_1,...,\mathbf{r}_N$ denote the coordinates of the electrons of the molecule and $\mathbf{r}$ that of the incoming electron. Φ_i is the wave function of the initial state of the molecule and $\exp\{i\mathbf{k}_i\cdot\mathbf{r}\}$ specifies the energy and the direction of the incident electron. The detection process is represented by the wave function $S_f = \Phi_f(\mathbf{r}_1,...,\mathbf{r}_N)\exp\{i\mathbf{k}_f\cdot\mathbf{r}\}$, where Φ_f is the electronic wave function of the molecule after collision and $\exp\{i\mathbf{k}_f\cdot\mathbf{r}\}$ describes the direction and the energy of the scattered electrons counted by the detector. The magnitude of $\mathbf{k}_f$ is given by the energy conservation condition

$$\mathbf{k}_f^2 - \mathbf{k}_i^2 = 2m(\epsilon_i - \epsilon_f)/\hbar^2 \quad (2.3)$$

(ϵ_f and ϵ_i are the energies of the states Φ_f and Φ_i); the direction of $\mathbf{k}_f$ is set by the position of the detector. This is complicated for inelastic processes. The function $\psi_i^{(+)}$ ($\psi_i^{(-)}$) is the stationary state created by the fact that the state S_i (S_f) is modified by the presence of the molecule. $\psi_i^{(+)}$ ($\psi_f^{(-)}$) satisfies the Lippmann–Schwinger equation with outgoing (incoming) boundary condition. These functions are expanded as linear combinations of $(N+1)$ electron Slater determinants composed of molecular orbitals expressed in terms of Cartesian Gaussian functions. Note that $\psi_i^{(+)}$ and $\psi_i^{(-)}$ are $(N+1)$ electron wave functions describing the state of the N target electrons plus the probing electron. Since $\psi_i^{(+)}$ and $\psi_i^{(-)}$ are antisymmetrized with respect to all $(N+1)$ coordinates, the calculation includes the electron–molecule interactions caused by the Pauli principle (i.e., exchange effects).

Details of the implementation of this method to obtain both elastic and electronically inelastic cross sections for H_2 have been discussed elsewhere.[55(b)] We note that in particular neither the muffin-tin approximation[59–61] nor the local exchange approximation[61] is assumed. In general, the theory also allows for the inclusion of both open and closed channels. This is why the potential V, customarily appearing in the Schwinger variational expression, is replaced in Eq. (2.1) by the term W, and the customary free Green's function is replaced by the projected Green's function

$$G_p^{(+)} = -\sum_\alpha \Phi_\alpha^*(\mathbf{r}_1,...,\mathbf{r}_N)\Phi_\alpha(\mathbf{r}_1,...,\mathbf{r}_N) \times\exp\{ik_\alpha|\mathbf{r}-\mathbf{r}'|\}/\{2\pi|\mathbf{r}-\mathbf{r}'|\}. \quad (2.4)$$

The sum is over those electronic states of the molecule which the electron can excite without violating energy conservation.

In these calculations we have used, for the electronically inelastic collisions, only two open channels, and do not obtain vibrationally resolved cross sections, i.e., we sum over the entire excitation band. This approximation can be easily improved by multiplying the transition amplitude with the Franck–Condon factors, i.e., with the overlap integrals

between the ground vibrational state and the vibrational states of the final electronic state of molecule. In the gas phase calculations the Franck–Condon correction is essential if one is interested in the shape of the loss peak as a function of energy. In surface science, however, we must also contend with the additional peak broadening mechanisms outlined in the Introduction. Therefore it does not seem worth computing the broadening caused by the nuclear motion alone if these other effects are left out.

B. The role of the surface

In principle there are two accurate ways of including the surface in the present calculations: one is to use in Eq. (2.1) the Green's function for the surface instead of the free-space Green's function $(-1/2\pi)\exp\{ik_f|\mathbf{r}-\mathbf{r}'|\}/|\mathbf{r}-\mathbf{r}'|$ appearing in Eq. (2.4); the other is to use in the present procedure a molecule consisting of the adsorbate and a metal cluster which incorporates most of the metal atoms that are likely to be sampled by the electron. Since we are only trying to evaluate how sensitive the differential cross section for electron scattering is to the orientation of H_2 and its final state, we avoid such extensive computations at this time and develop the simplified treatment of surface effects presented below.

The model can be introduced heuristically by considering the processes depicted in Fig. 1 and represented by the transition amplitude

$$f(\mathbf{k}_f\leftarrow\mathbf{k}_i)+f(\mathbf{k}_i\leftarrow\bar{\mathbf{k}}_i)R(\mathbf{k}_i)+R(\bar{\mathbf{k}}_f)f(\bar{\mathbf{k}}_f\leftarrow\mathbf{k}_i)+R(\bar{\mathbf{k}}_f)f(\bar{\mathbf{k}}_f\leftarrow\bar{\mathbf{k}}_i)R(\mathbf{k}_i). \quad (2.5)$$

Here $f(\mathbf{k}_f\leftarrow\mathbf{k}_i)$ is the amplitude of the transition from S_i to S_f [as defined by Eq. (2.1)] for the electron–molecule collision. $R(\mathbf{k}_i)$ is the reflection coefficient for an electron with momentum $\mathbf{k}_i$ which is scattered by the flat surface. The first term in Eq. (2.5) represents the contribution to the total scattering amplitude from electrons which collide with the molecule only and are backscattered into the detector. The second term in Eq. (2.5) represents the contribution of the process shown in Fig. 1(b). The electron first collides with the flat surface and then with the molecule. The first collision results in a change of wave vector from $\mathbf{k}_i\equiv(k_{ix},k_{iy},k_{iz})$ to $\bar{\mathbf{k}}_i\equiv(k_{ix},k_{iy},-k_{iz})$ (i.e., specular scattering). Since the surface is an imperfect mirror the probability amplitude for this backscattering process is $|R(\mathbf{k}_i)|^2$. The electron deflected by the surface then collides with the molecule. The transition amplitude for this collision is $f(\mathbf{k}_f\leftarrow\bar{\mathbf{k}}_i)R(\mathbf{k}_i)$. Similarly, the third and the fourth terms in Eq. (2.5) correspond to the processes shown in Figs. 1(c) and 1(d).

The reflection coefficient $R(\mathbf{k})$ can be calculated from a simple model which assumes that the scattering of the electron by the metal is due to a step potential whose energy is zero in vacuum and $-V_0$, $V_0>0$ in the metal. This leads to

$$R(\mathbf{k})=(|k_z|-k_z')(|k_z|+k_z')^{-1}\exp\{2i|k_z|z_0\} \quad (2.6)$$

with

$$k_z'=\sqrt{k_z^2+2mV_0/\hbar^2}\,. \quad (2.7)$$

Here k_z is the wave vector component perpendicular to the surface and z_0 is the distance from the center of mass of the molecule to the surface. The origin of the coordinate system is in the center of mass and the plane xOy is parallel to the surface. The Oz axis points towards the vacuum.

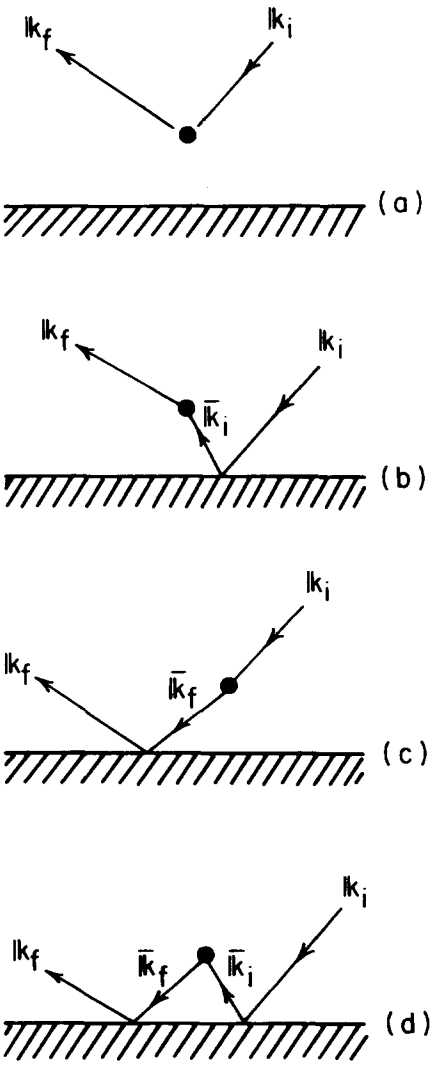

FIG. 1. Schematic drawing of the scattering processes of a molecule adsorbed on surface by low energy electrons. (a) The electron is scattered by the molecule only; (b) the electron hits the surface before being scattered by the molecule; (c) the electron is scattered by the molecule before being reflected by surface; (d) the surface scatters the electron before and after the electron–molecule collision.

Note that it is possible to use the results of electron–surface scattering experiments to measure $|R(\mathbf{k})|^2$. One can also use better models to compute R. However since the manner in which the presence of the surface is introduced in the calculation is semiquantitative, it is reasonable to use a simple semiquantitative choice of R.

It is instructive to examine more carefully the nature of the approximations introduced when Eq. (2.5) is used. To do this we start from the two potential formula[61] in which the specular contribution has been omitted, i.e.,

$$\langle f|\tau|i\rangle=\langle\phi_{f,s}^{(-)}|V|\psi_i^{(+)}\rangle, \quad (2.8)$$

where τ is the T matrix, $\psi_i^{(+)}$ is the exact scattering wave function (including the effects of the molecule and the sur-

face), and $\phi_{f,s}^{(-)}$ is given by

$$\phi_{s,f}^{(-)} = S_f + G_0^{(-)}(E^f) V_s \phi_{s,f}^{(-)} . \tag{2.9}$$

Here $G_0^{(-)}(E_f) = (E_f - H_0 - i\eta)^{-1}$, where H_0 is the kinetic energy operator of the electron, $G_0^{(-)}$ is the free-electron Green's funtion with incoming boundary conditions, and V_s is the electron surface interaction. The wave function $\psi_i^{(+)}$ satisfies

$$\psi_i^{(+)} = \phi_{i,s}^{(+)} + G_s^{(+)}(E_i) V \Psi_i^+ , \tag{2.10}$$

where $G_s^{(+)} = (E_f - H_0 - V_s - i\eta)^{-1}$ is the Green's function of the electron–surface Hamiltonian with an outgoing boundary condition and V is the electron–molecule interaction.

Since these equations are exact we must make some approximations to obtain Eq. (2.5). The first is to replace $G_s^{(+)}(E_i)$ in Eq. (2.10) with $G_0^{(+)}(E)$. Physically this means that the surface influences the state of the electron either before or after it interacts with the molecule, but not during the electron–molecule collision. As a result of this approximation we can write $V|\psi_i^{(+)}\rangle = T|\phi_{i,s}^{(+)}\rangle$ where T is the T matrix for the electron–molecule collision, and thus rewrite Eq. (2.8) as

$$\langle f|\tau|i\rangle \simeq \langle \phi_{f,s}^{(-)}|T|\phi_{i,s}^{(+)}\rangle . \tag{2.11}$$

Using the definition of the Moller operators[62]

$$\Omega_s^{(\pm)} = 1 + G_s^{(\pm)}(E) V_s$$

and the equations $\phi_{s,f}^{(-)} = \Omega_s^{(-)}(E_f) S_f$ and $\phi_{s,i}^{(+)} = \Omega_s^{(+)} S_i$ we can rewrite Eq. (2.11) as

$$\begin{aligned}\langle f|\tau|i\rangle = {} & \langle S_f|T|S_i\rangle + \langle S_f|T|V_s G_s^{(+)}(E_i) S_i\rangle \\ & + \langle V_s G_s^{(-)}(E_f) S_f|T|S_i\rangle \\ & + \langle V_s G_s^{(-)}(E_f) S_f|T|V_s G_s^{(+)}(E_i) S_i\rangle .\end{aligned} \tag{2.12}$$

To interpret these terms physically, we note that $V_s G_s^{(+)}(E_i) S_i = \Phi_i(\mathbf{r}_1,\ldots,\mathbf{r}_N) V_s G_s^{(+)}(E_i) \exp\{i\mathbf{k}_i\cdot\mathbf{r}_i\}$ is the initial state electronic wave function multiplied by the outgoing wave created by scattering of the incident plane wave by the surface. This is by definition equal to $R(\mathbf{k}_i)\Phi_i(\mathbf{r}_i,\ldots,\mathbf{r}_N)\exp\{i\mathbf{k}_i\cdot\mathbf{r}_i\}$. Thus the second term in Eq. (2.12) leads to

$$R(\mathbf{k}_i) \int d\mathbf{r}_1,\ldots,d\mathbf{r}_N \Phi_f^*(\mathbf{r}_1,\ldots,\mathbf{r}_N)\exp\{-i\mathbf{k}_i\cdot\mathbf{r}_i\} T \times \Phi_i(\mathbf{r}_1,\ldots,\mathbf{r}_N)\exp\{\mathbf{k}_i\cdot\mathbf{r}\} d\mathbf{r}$$

which is proportional to the term $f(\mathbf{k}_f \leftarrow \bar{\mathbf{k}}_i) R(\mathbf{k}_i)$ appearing in Eq. (2.5). The other terms in Eq. (2.12) lead in a similar manner to the terms of Eq. (2.5).

The method discussed above leaves out the "image effects" which often play a prominent role in simplified modes. This effect is heuristically introduced by arguing that if the incoming electron interacts with a molecular dipole it also must, according to phenomenological electrodynamics, interact with its image with respect to the surface plane. First, as we have already argued, the physical picture of an electron interacting with a dipole is not valid under the conditions prevalent in the current experiments. Second, the image formula is based on phenomenological electrodynamics

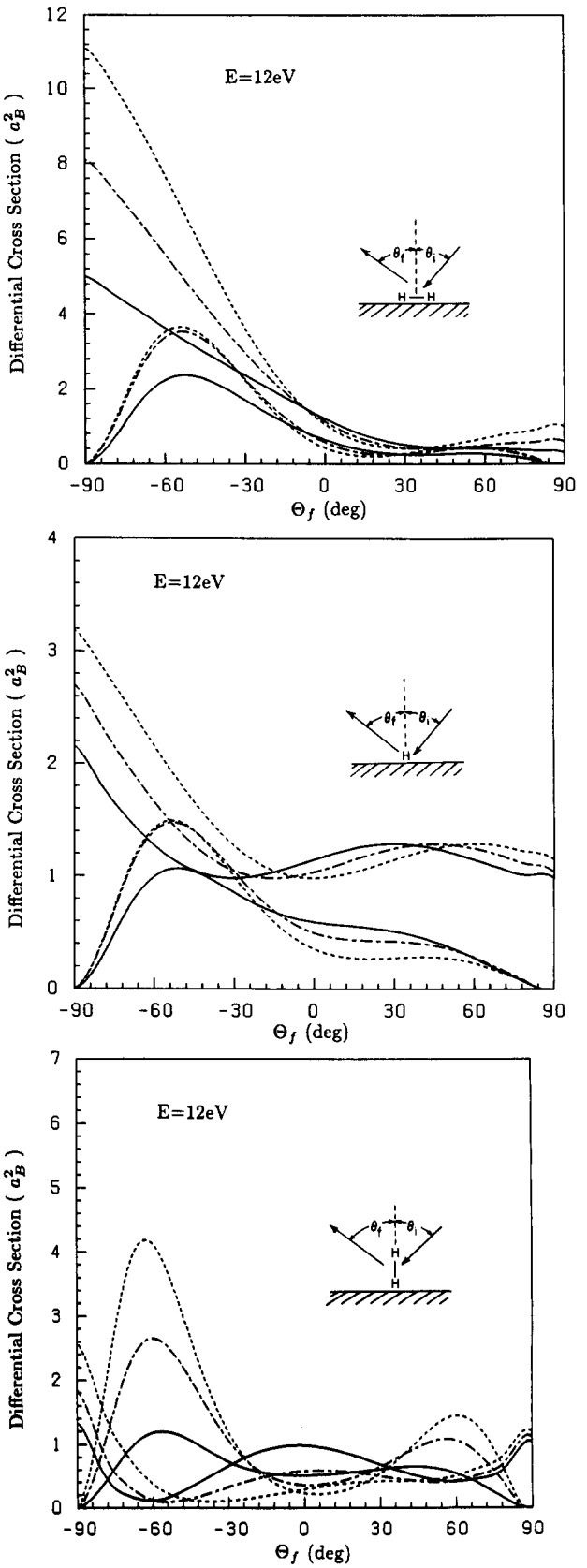

FIG. 2. Differential cross section for the elastic scattering by a H_2 molecule adsorbed on a surface. The incident energy is 12 eV. The scattering geometry is shown in the insert. – $\Theta = 30°$; – · – · $\Theta = 45°$; --- $\Theta = 60°$. (a) H_2 is parallel to the surface with the molecular axis in the plane of incidence of the electron. (b) H_2 is parallel to the surface with the molecular axis perpendicular to the plane of incidence. (c) H_2 is normal to the surface with the molecular axis in the plane of incidence. We plot the cross sections for scattering in the presence and in the absence of the surface. The results for the former are those with zero cross section at $\Theta_f = \pm 90°$.

which assumes that the dielectric response is local and that the dielectric constant has a discontinuity at the surface. Both these assumptions break down for oscillating charges located at a small distance from the surface, for both zero[42] (i.e., elastic collisions) and high frequency[43] (i.e., electronic excitations) oscillators. It is therefore not clear that incorporating "image" forces is an improvement over the present calculation. For this reason we decided to omit them even though it is not difficult to include in the theory an external field which would mimic the influence on the electron of the electric polarization of the metal surface by the adsorbate.

III. RESULTS

In what follows we present the results of our calculations of the differential cross section for the excitation of a H_2 molecule located near a surface with the work function of Al. The differential cross section is given by

$$\frac{d\sigma}{dr} = (k_f/k_i)|\langle f|\tau|i\rangle|^2, \tag{3.1}$$

where the transition amplitude $\langle f|\tau|i\rangle$ is given by Eq. (2.5), the molecular amplitude $f(\mathbf{k}_f \leftarrow \mathbf{k}_i)$ by Eq. (2.1), and the reflection coefficient by Eq. (2.6). The molecular scattering cross sections were obtained using the procedure of Berscansin, Lima, Huo, and McKoy.[55(b)] In Fig. 2 we plot differential cross sections for elastic scattering; Fig. 3 shows inelastic scattering cross sections for the transitions $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$; Fig. 4 displays differential cross sections for the $X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$ transition. All the plots show the dependence of the differential cross sections on the detection angle, for three angles of incidence. Both the molecular cross sections [i.e., using the amplitude given by Eq. (2.1)] and the cross sections in the presence of the surface are shown in each graph. In all cases we consider three situations: (a) H_2 lies down on the surface with the molecular axis in the plane of incidence of the electron; (b) H_2 lies down on the surface with the molecular axis perpendicular to the plane of incidence; (c) H_2 stands up, perpendicular to the surface.

The main questions raised here are whether the cross sections are different enough to permit us to distinguish experimentally between the "lying down" and the "standing up" orientations, and to identify the nature of the final electronic state. To facilitate the analysis we have summarized in Table I the main features of the angular dependence of the differential cross sections (in the presence of the surface). Let us now examine Table I to see whether we can determine the orientation of the molecule from the scattering data. If we examine the angular distribution of the electrons which have excited H_2 from $X\,^1\Sigma_g^+$ to $a\,^3\Sigma_g^+$ we find a substantial difference between the two configurations: if H_2 stands up there is one loss peak, located between the normal direction and the specular one; as the angle of incidence is increased this loss peak moves towards the normal and its intensity goes down. If H_2 lies down in the plane of incidence of the electrons, the angular distribution of the loss peak is very different: for angles of incidence higher than 90° the intensity of the loss feature peaks at two final angles; as the incident angle is increased these final angles (at which the loss intensity peaks) move towards the normal to the surface and their

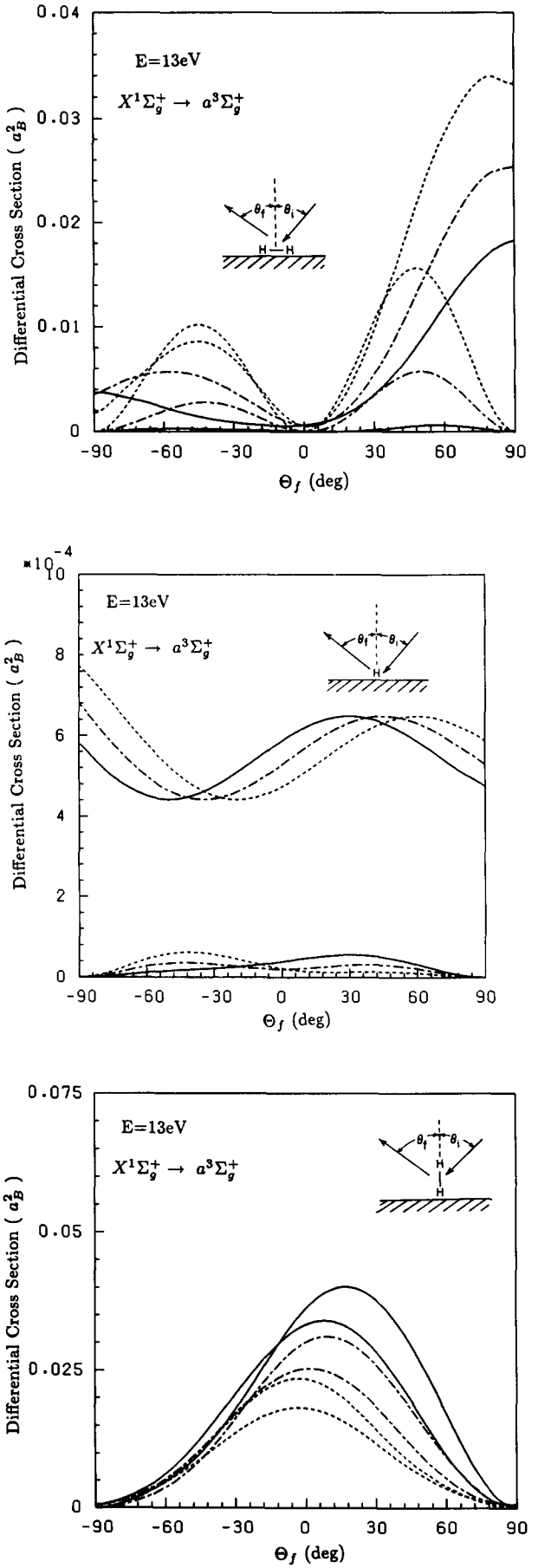

FIG. 3. Differential cross sections for the excitation of the $a\,^3\Sigma_g^+$ state of an H_2 molecule adsorbed on surface. The incident energy is 13 eV. Other information is identical to that of Fig. 2.

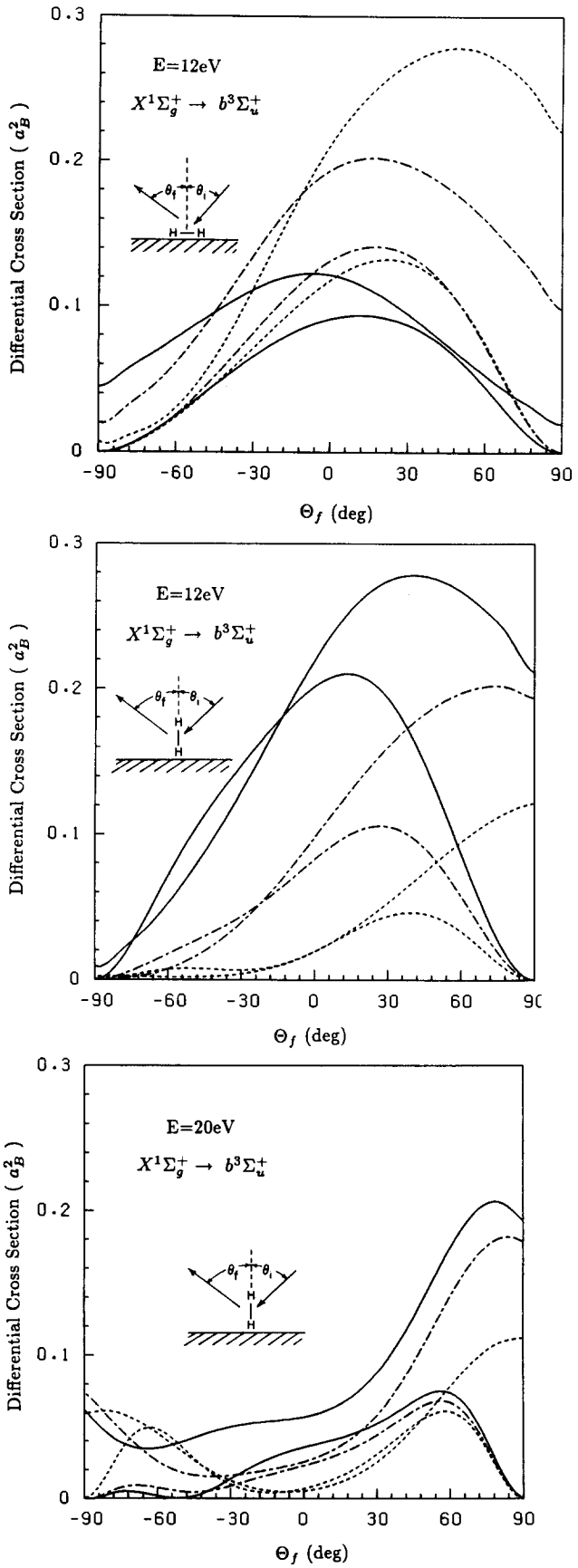

FIG. 4. Differential cross sections for the excitation of the $b\ ^3\Sigma_u^+$ state of an H_2 molecule adsorbed on a surface. (a) H_2 is parallel to the surface with axis in the plane of incidence. The energy of incidence is 12 eV. (b) H_2 is normal to the surface with axis in the plane of incidence. The incident energy is 12 eV. (c) H_2 is normal to the surface with the axis in the plane of incidence. The incident energy is 20 eV.

intensity goes up. Thus the presence of the double-peaked feature fingerprints the lying down position. Furthermore, if the sample is rotated so that the axis of the molecule is perpendicular to the plane of incidence of the electrons, the two-peak feature flattens out to become a broad peak. For the standing molecule such a sample rotation causes no change in the angular distribution.

To further increase the reliability of the diagnostics one can, in addition, examine the angular distribution of the electrons scattered elastically. In this case one must avoid the specular direction where most of the electrons scattered elastically by the surface will go. For the case of the standing molecule, measurements at an incident angle of 45° are useful since they give two peaks, at 60° and $-60°$, with the intensity at $-60°$ twice as large as that at 60°. The lying down molecule gives one peak at 50°, for all positions (i.e., molecular axis in the plane of incidence of the electrons or perpendicular to it). The intensities depend weakly on the angle of incidence and go down by a factor of 2 when the molecule is rotated out of the plane of incidence (no such change occurs for the standing molecule).

Finally, if further reassurance is needed one can look at the loss peak caused by the excitation $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$. Both the standing and the lying-down molecule give one broad peak and their behavior is rather similar. Luckily there is a selection rule[55(b)] for the lying down molecule whose axis is perpendicular to the plane of incidence and the intensity of inelastic scattering is zero. Thus the rotation of the sample will lead to a dip in the cross section for the lying-down molecule and to no change for the standing one.

Of course the observed spectra will differ from the predicted ones due to the approximate treatment of the scattering by the surface and various imperfections of the experimental setup. We feel however that the gross features predicted here will not be washed out and that the differences between the two molecular positions can be identified by the experiments suggested here with a great degree of reliability.

It is interesting to note that the excitations considered here are dipole forbidden, because the final states are triplets. In other words if the dipole rules were valid (i.e., if Born approximation is valid, the exchange interaction is negligible, the momentum transfer is small, and the contribution of the molecular backscattering events to the near specular flux is negligible as compared to the forward scattering ones) the cross sections would be strictly zero, regardless of the molecular orientation of the molecule.

Finally, we examine our results (Table I) to see whether the dependence of the differential cross section on the detection angle can be used to establish the nature of the final states. If the molecule is standing up, both final states lead to one peak in the angular distribution. If the final state is $a\ ^3\Sigma_g^+$ the peak moves towards the normal as the incidence angle is increased. For $b\ ^3\Sigma_u^+$, the peak moves away from the normal, as the angle of incidence is increased. It is thus possible to distinguish between these states by using differential cross section measurements.

Figures 2–4 also compare the scattering by an oriented gas phase molecule (in the absence of the surface), to that

TABLE I. A summary of the main results concerning the dependence of the total loss intensity on the detection angle. The table gives the final angles for which the loss intensity has peaks and the magnitude of the differential cross section for that angle. For example, for the transition $X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$, for an angle of incidence of 45° and incident energy of 13 eV, for H_2 with the axis parallel to the surface and perpendicular to the plane of incidence, the cross section has two peaks: one at a final angle of $-60°$ and the other at a final angle of 50°. The cross section for the first peak is 0.005 Å^2 and the one of the second peak is 0.007. The definitions of the angles are those shown in Figs. 2–4. Another example: the cross section for the loss peak corresponding to the transition $^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$, normal to the surface for H_2, for an angle of incidence of 30° and an incident energy of 20 eV, has a peak at a detection angle of 60° and the cross section is ~0.05 Å.

Transition	Angle of incidence (deg)	E_i (eV)	(b) H_2 parallel to surface with axis perpendicular to the plane of incidence	(a) H_2 parallel to surface with axis in the plane of incidence	H_2 normal to surface
	30	12	−50°(2.2); one peak	−50°(1) shoulder 45°	−60°(1.2) shoulder at 50°
$X\,^1\Sigma_g^+ \rightarrow X\,^1\Sigma_g^+$	45	12	−50°(3.6); one peak	−50°(1.45)	−60°(2.6); 60°(1.1)
	60	12	−50°(3.6); one peak	−50°(1.45)	−60°(4.1); 60°(1.4)
	30	13		flat ($0.6.10^{-4}$)	25°(0.04)
$X\,^1\Sigma_g^+ \rightarrow a\,^3\Sigma_g^+$	45	13	−60(0.005); 50(0.007)	rather flat	12°(0.0325)
	60	13	−45(0.01); 45(0.017)	rather flat	0°(0.025)
	30	12	15°(0.08) one broad peak	0	15°(0.2) is a broad peak
$X\,^1\Sigma_g^+ \rightarrow b\,^3\Sigma_u^+$	45	12	15°(0.14) one broad peak	0	30°(0.1) is a broad peak
	60	12	25°(0.13) one broad peak	0	45°(0.05) is a broad peak
	30	20	60°(0.05); one peak		60°(0.05); one peak
	45	20	60°(0.05); one peak		60°(0.05); one peak
	60	20	60°(0.05); one peak		60°(0.05); −60(0.05)

obtained by incorporating the surface in the manner described in Sec. II. In all the figures the results pertaining to the oriented molecule (gas phase) can be identified as those whose cross section is finite (i.e., nonzero) at $\theta_f = 90°$ and $-90°$. It is easy to see that the presence of the surface alters substantially the dependence of the cross section. The main physical mechanism for this alteration is interference. For example, if the detection angle approaches $\pm 90°$, the reflection coefficient R approaches -1; in Eq. (2.5), the amplitude $f(\mathbf{k}_f \leftarrow \mathbf{k}_i)$ is canceled by $R(\bar{\mathbf{k}}_f) f(\bar{\mathbf{k}}_f \leftarrow \mathbf{k}_f)$, and $f(\mathbf{k}_f \leftarrow \bar{\mathbf{k}}_i) R(\mathbf{k}_i)$ is canceled by $R(\bar{\mathbf{k}}_f \leftarrow \bar{\mathbf{k}}_i) R(\mathbf{k}_i)$; these cancellations lead to a zero differential cross section at $\theta_f = \pm 90$.

Interference also leads to dependence of the scattering amplitude on the distance between the molecule and the surface barrier at which most of electron reflection occurs. This distance enters Eq. (2.5) through the reflection coefficients $R(\mathbf{k})$, given by Eq. (2.6). Since in a realistic model it is difficult to define this distance accurately, we carried out calculations with several reasonable values for this distance to show that the angular patterns on which the analysis of the molecular orientation and the determination of the final wave function are based are not altered qualitatively when the distance is changed within a reasonable range.

An examination of Figs. 2–4 shows that the reflecting properties of the surface must be incorporated in electron scattering calculations; a calculation of scattering by an oriented molecule with no surface leads to false angular distributions. On the other hand, the simple reflection model used here is likely to exaggerate the sharpness of the dependence of the differential cross section on the angles of detection and incidence. If, for example, we incorporate in the calculation the fact that we do not know the precise location z_0 of the reflection plane by treating z_0 as a stochastic variable, we must average the cross section over z_0; this will reduce the sharpness of the angular dependence.

Before concluding this analysis we emphasize again that this is a model study whose main purpose is to uncover whether there are pronounced useful trends in the angular dependence of the differential cross section. We use H_2 for computational simplicity and because it is a nearly spherical molecule and thus provides a stringent test of the ability of the electron to probe molecular orientation. The treatment of the surface is crude, but we believe that the pronounced trends predicted by this model are likely to persist if a more realistic treatment of the surface is used. We do not expect that our conclusions can be tested experimentally since chemisorbed H_2 dissociates and the physisorbed H_2 is likely to rotate freely. We are currently performing computations for CO, N_2, NH_3, and H_2O and those results can be submitted to an experimental test.

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